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Zirconium Complexes

Synthesis, Structural Characterization, and Quantitative Basicity Studies of Lithium Zirconimidate Complexes**

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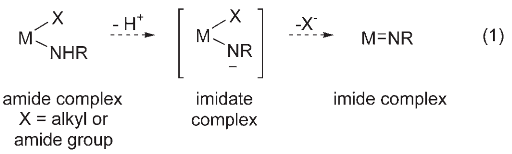
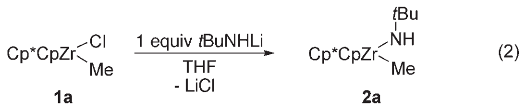
Monomeric, early-transition-metal imide complexes [M=NR], which mediate numerous catalytic and stoichiometric nitrogen-transfer reactions,[1a] can be prepared by α abstraction and extrusion of a good leaving group (e.g. alkane or amine) from a metal amide species [X−M−NHR].[1] These α-abstraction reactions are thought to be concerted,[1] but in a hypothetical stepwise process, a potential intermediate is an imidate complex $[M{-}NR]^-$ [Eq. (1)]. The ease with which

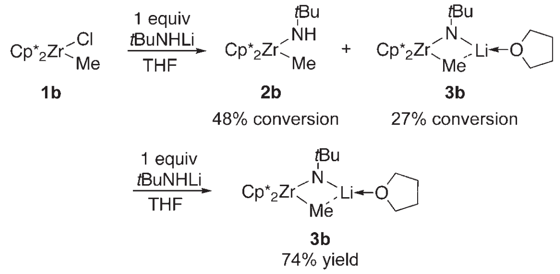


such imidate species can be observed and isolated depends upon the absence of a good leaving group on the metal and on the acidity of the N−H proton. There are few reports of such deprotonation reactions in the literature;[2] the resultant imidates are either stabilized by adjacent conjugating groups[2a–c] or readily undergo subsequent reactions, thus preventing their structural characterization.[2d] We report herein the formation and structural characterization of monomeric, nonconjugatively stabilized lithium zirconocene imidate complexes.

In our ongoing studies on early-metal imide complexes, we became interested in preparing a series of substituted zirconocene methyl amide complexes as precursors to imidozirconocene complexes.[1] In systems with relatively small ancillary ligands on zirconium, such as Cp*Cp ($Cp = \eta^5$-C_5H_5, $Cp^* = \eta^5$-C_5Me_5), methyl amide complexes such as **2a** could be accessed through salt metathesis [Eq. (2)]. When $[Cp^*_2Zr(Me)(Cl)]$ (**1b**) was subjected to the same reaction conditions, however, incomplete consumption of **1b** and a mixture of two new products were observed (75% conversion based on **1b**). These products were tentatively assigned as methyl amide complex **2b** (48% conversion based on **1b**) and



lithium zirconimidate complex **3b** (27% conversion based on **1b**). Upon addition of a second equivalent of *t*BuNHLi, only complex **3b** was observed and subsequently isolated in 74% yield (Scheme 1).



Scheme 1. Reaction of complex **1b** with *t*BuNHLi.

The identity and structural features of complex **3b** were elucidated by NMR spectroscopy and X-ray crystallography. The ^{1}H NMR spectrum of complex **3b** lacks a diagnostic N−H peak, and the zirconium methyl signal is shifted upfield ($\delta = -0.75$ ppm) relative to the corresponding signal in complex **2b** ($\delta = -0.19$ ppm). Further ^{7}Li-^{13}C and ^{6}Li-^{1}H NMR correlation experiments yielded measurable coupling constants (12 Hz[3] and 2.3 Hz, respectively), thus indicating that the {Me−Li} fragment is intact in solution.

X-ray crystallography revealed that the atoms comprising the metallacycle (Zr-N-Li-C) are coplanar (Figure 1).[4] The Zr−C bond length of 2.36 Å is consistent with a Zr−C single bond,[5] and the positions of the hydrogen atoms on C1 were calculated. The Zr−N bond length (r_{Zr-N}) of 1.91 Å indicates a high bond order, suggesting that zirconimidate **3b** could be an intermediate structure between a zirconocene amide ($r_{Zr-N} =$ 2.05–2.08 Å, R = alkyl)[6] and a zirconocene imide ($r_{Zr=N} =$ 1.85–1.88 Å, R = alkyl).[1b] Both NMR spectroscopic and crystallographic data indicate a bond between the $\{Zr{-}CH_3\}$ moiety and lithium. Either σ donation from the Zr−C bond or from one or two of the C−H bonds in a rapidly rotating methyl group would be consistent with these data.

Analogous lithium zirconimidates (**3c–e**) were prepared by treating the corresponding methyl chlorides with 12 equiv *t*BuNHLi in THF solution (Scheme 2). Complexes **3b** and **3e** were also obtained in comparable yields by treating the

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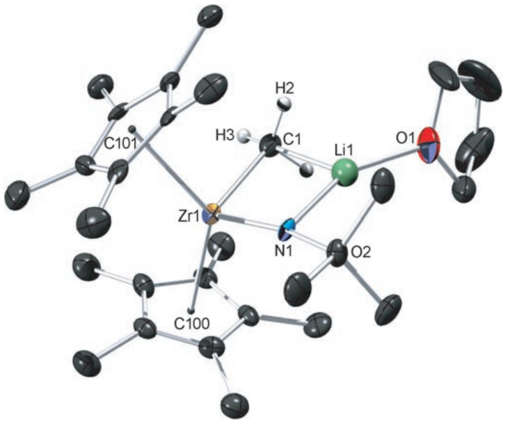
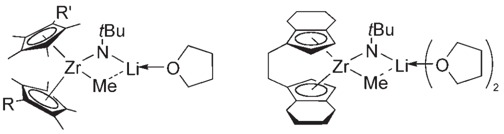


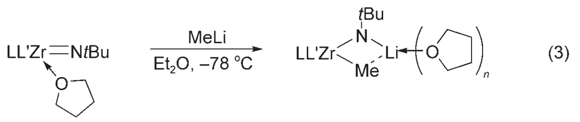
Figure 1. X-ray crystal structure of **3b** with thermal ellipsoids drawn at the 50% probability level; most hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zr1–N1 1.909(4), Zr1–C1 2.358(5), C1–Li1 2.17(1), N1–Li1 2.01(1), Zr1–C100 2.3763(5), Zr1–C101 2.3589(5), Li1–O1 1.88(1), N1–C2 1.473(6); Zr1-N1-Li1 91.1(3), Zr1-C1-Li1 76.1(3), C1-Li1-N1 98.1(5), Zr1-N1-C2 167.0(3), C101-Zr1-C100 127.95(2).



3c: R = H, R' = Me; (Cp*Cp^{Me4}); 86% yield (Cp^{Me4} = η^5-C_5Me_4H)
3d: R = R' = H; (Cp$^{Me4}_2$); 64% yield
3e: *rac*-(ebthi); 53% yield

Scheme 2. Isolated lithium zirconimidate complexes.

corresponding imidozirconium complexes with one equivalent of methyllithium [Eq. (3)]. Lithium zirconimidates **3b–e**



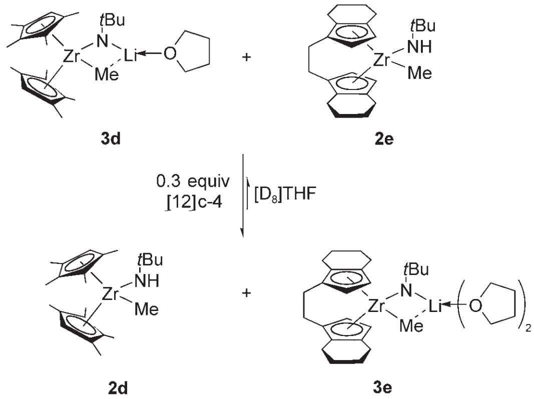
4b: LL' = Cp*$_2$
4e: LL' = *rac*-(ebthi)
3b: LL' = Cp*$_2$; *n* = 2; 75% yield
3e: LL' = *rac*-(ebthi); *n* = 1; 45% yield

may therefore be thought of as either deprotonated amide species or alkyllithium adducts of zirconium imide complexes. Complexes **3b–e** were thermally unstable and extremely sensitive to air and water. Efforts to isolate other zirconimidate complexes with smaller ancillary ligands or other substituents on the amide nitrogen atom were unsuccessful (see the Supporting Information).

The isolation of zirconimidate complexes **3b–e** presented an opportunity to examine quantitatively the acidity of the N–H proton in methyl amide complexes **2b–e** (Scheme 3). We established the relative acidities of two methyl amide complexes, **2d** and **2e**, by a direct competition experiment (Scheme 4). Deprotonated amide complex **3d** was treated with methyl amide **2e** and 0.3 equiv [12]crown-4. In the absence of [12]crown-4, the acid–base reactions were

2b: R = R' = Me; (Cp*$_2$)
2c: R = H, R' = Me; (Cp*Cp^{Me4})
2d: R = R' = H; (Cp$^{Me4}_2$)
2e: *rac*-(ebthi)

Scheme 3. Methyl amide complexes **2b–e**.

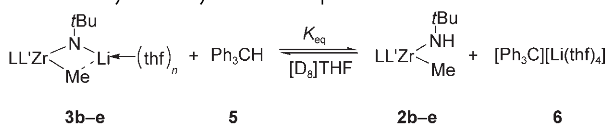


Scheme 4. Direct competition experiment between methyl amide complexes **2d** and **2e** ($K_{eq} = 12.9 \pm 0.6$).

extremely slow. The mixture was allowed to attain equilibrium over three days, at which point an equilibrium constant of 12.9 ± 0.6 was measured. Unfortunately, other combinations of methyl amide and zirconimidates yielded inconclusive results owing to the thermal instability of the imidate complexes.

To gauge the basicities of all four zirconimidate complexes, **3b–e** were treated with various Brønsted acids. When treated with [12]crown-4 and acids such as ammonium salts, phenylacetylene, or fluorene, complexes **3b–e** underwent quantitative protonation to yield methyl amide complexes **2b–e**. However, when complexes **3b–e** were treated with triphenylmethane and [12]crown-4, a mixture of **2–3** and **5–6** (see Table 1) was observed. These reactions were slow at room temperature, requiring two to three days to achieve equilibrium. Equivalent equilibrium constants could be

Table 1: Acidity of methyl amide complexes **2b–e**.[a]



Entry	Complex	Ligand	Yield [%][b]	K_{eq}[c]	$(pK_a)_{THF}$
1	**2b**	Cp*$_2$	33	0.249 ± 0.007	29.8
2	**2c**	Cp*Cp^{Me4}	42	0.524 ± 0.010	30.1
3	**2d**	Cp$^{Me4}_2$	51	1.05 ± 0.03	30.4
4	**2e**	*rac*-(ebthi)	22	0.079 ± 0.005	29.3

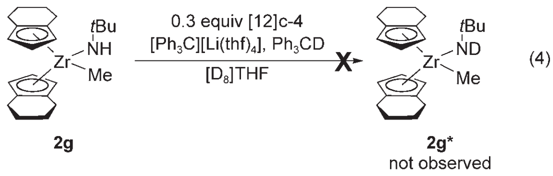
[a] Reactions were run with 0.3 equiv [12]crown-4. [b] Yield determined by NMR spectroscopy and calculated using 1,3-dimethoxy-5-methylbenzene as an external standard. [c] Values are reported as the average of three runs ± standard deviation.

obtained either by addition of **5** to **3** or by addition of **6** to **2**; the composition of the equilibrium mixture was not concentration-dependent. Equivalent equilibrium constants were measured from reaction mixtures containing either 0.3 or 1.0 equiv [12]crown-4. These results indicate that the addition of [12]crown-4 to the acid–base reaction mixtures affects the rates at which the reactions proceed but does not perturb the equilibria of these reactions.

Given the pK_a of triphenylmethane in THF (30.4),[7] pK_a values for the N−H proton in methyl amide complexes **2b**-**e** were extrapolated. A narrow range of values from 29.3 to 30.4 was observed (Table 1). The individual pK_a values measured for complexes **2d** and **2e** are consistent with the K_{eq} value measured in the direct competition experiment (Scheme 4). The *ansa*-bridged *rac*-(ebthi) complex **2e** was the most acidic amide complex of those examined (entry 4). However, the *ansa* ligand in complexes **2e** and **3e** renders the structures of these complexes quite different from those of non-*ansa* complexes **2b–d** and **3b–d**. For example, while *rac*-(ebthi) zirconimidate complex **3e** is solvated by two THF molecules, non-*ansa* zirconimidate complexes **3b–d** are solvated by only one THF molecule each. It is therefore difficult to draw direct comparisons between complexes **2e** and **2b–d**.

Curiously, complexes with bulkier ancillary ligands possessed more acidic N−H amide protons than their smaller congeners, contrary to the expected trend based on electronic arguments alone.[8] Addition of one methyl group to the ancillary cyclopentadienyl ligands (e.g. Cp*Cp^{Me4} to Cp^*_2) correlates to a three-fold increase in the acidity of the distant N−H amide proton (Table 1, entries 1–3). These results suggest that the acidity trend in methyl amide complexes **2b–d** might represent a rare example of "steric acidity."[9] That the observed pK_a differences are small is consistent with the fact that the X-ray crystal structures of **3b** and **3d** show little structural variation between the two complexes (Figure 2).

While the protonation of complexes **3b–e** with Ph_3CH appears to be under thermodynamic control, we carried out an isotope exchange experiment to determine whether the deprotonation of methyl amide complexes with other ancillary ligands was disfavored due to thermodynamics or kinetics. Methyl amide complex **2g**, which did not undergo observable deprotonation when treated with *t*BuNHLi, was treated with triphenylmethane deuterated at the methine position, triphenylmethyl(lithium), and [12]crown-4 [Eq. (4)]. No deuterium incorporation at the N−H position was observed over three days, indicating that the deprotonation



of **2g** has a high kinetic barrier. Thus, the deprotonation reactions of zirconium methyl amide complexes can have variable kinetic and thermodynamic profiles depending upon which ancillary ligand is coordinated to zirconium. These results demonstrate a complex relationship between ancillary ligand sterics and the acidity of the amide N−H proton.

In summary, a new class of zirconium–nitrogen species has been isolated and structurally characterized. Arising from either deprotonation of zirconium methyl amide complexes or addition of methyllithium across the zirconium imide moiety, zirconimidate complexes become decreasingly basic as their ancillary ligands become bulkier. While these basicity studies highlight the behavior of zirconimidate complexes as Brønsted basic, deprotonated amide complexes, further studies addressing the reactivity of zirconimidate complexes with other organic substrates may provide insight into their potential use as nucleophiles and nitrogen-transfer reagents.

Figure 2. Superimposed X-ray crystal structures of **3b** (red) and **3d** (black). Hydrogen atoms are omitted for clarity.

Experimental Section

General procedure for preparing zirconimidate complexes: In an N_2-filled glovebox, a 20-mL scintillation vial was equipped with a magnetic stir bar and charged with a solution of the [LL′Zr(Me)(Cl)] complex (0.2 mmol, 1 equiv) and *t*BuNHLi (2.4 mmol, 12 equiv) in THF (20 mL). The clear, yellow reaction mixture was stirred for 5–8 h at ambient temperature. The solvent was removed in vacuo, and the resulting residue was then extracted with pentane (3 × 4 mL). The combined pentane extracts were filtered, concentrated, and cooled to −30 °C. Products were obtained as colorless or yellow crystalline solids (53–86 %).

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[3] The {ZrMeLi} signal of the ^{7}Li-^{13}C HMQC spectrum contained an extraneous artifact. When the ^{7}Li-^{13}C correlation experiment was performed on complex **3d**, no artifact and a comparable coupling constant ($^{1}J_{^{7}Li\text{-}^{13}C} = 10$ Hz) were observed.

[4] a) Crystal data for **3b**: $ZrONC_{29}LiH_{50}$, $M_r = 526.88\ g\,mol^{-1}$, $0.20 \times 0.15 \times 0.09\ mm^3$, monoclinic, space group $P2_1/c$, $a = 9.6663(8)$, $b = 18.721(2)$, $c = 16.278(1)$ Å, $\beta = 104.103(1)°$, $V = 2857.0(4)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.225\ g\,cm^{-3}$, $\mu = 4.04\ cm^{-1}$, $F(000) = 1128.00$, 13069 reflections measured, 2565 unique [$R(int) = 0.051$], $2\theta_{max} = 49.4°$, 293 refined parameters, $R_1 = 0.046$ (2807 observations where $I > 3.00\sigma(I)$), $wR_2 = 0.046$, GoF = 1.46. Data were collected at 103(2) K on a Siemens SMART CCD diffractometer (Bruker SMART v.5.059, Area-Detector Software Package, Bruker AXS, Inc., Madison, WI, 1995–1999) with graphite monochromated $Mo_{K\alpha}$ radiation using ω scans (0.3° per 10.0-s frame). All non-hydrogen atoms were refined anisotropically except for the lithium atoms, which were refined isotropically. Hydrogen atoms were included but not refined. The maximum and minimum peaks on the final difference Fourier map corresponded to 0.59 and $-0.72\ e\,Å^{-3}$, respectively. General methods for integration, solution, and refinement can be found in the Supporting Information. CCDC 682892 (**3b**) and 682893 (**3d**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif (see the Supporting Information).

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